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5. AUTHOR(s)
Terry L. Thiem, Lyn R. Watson, James A. Gardner, Rainer
R. Dressler, Richard H. Salter, Edmond Murad

6. PERFORMING ORGANIZATION NAME AND ADDRESS(es)
Phillips Lab/WSSI
29 Randolph Road
Hanscom AFB, MA 01731-3010

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EVALUATION OF THE LASER ABLATION OF TRANSITION METALS/METAL COMPOUNDS BY TIME-OF-FLIGHT AND OPTICAL SPECTROSCOPY

Terry L. Thiem, Lyn R. Watson, James A. Gardner, Rainer A. Dressler, Richard H. Salter and Edmond Murad
Spacecraft Interactions Branch, Phillips Laboratory, Hanscom AFB, MA

ABSTRACT

A fast pulsed beam of neutral metal atoms is produced by laser vaporization of a solid metal or metal compound sample in a modified high-temperature mass spectrometer. Atomic beams of several eV kinetic energy are generated as measured using time-of-flight spectroscopy. The energy range can be controlled with the laser power, similar to studies conducted on thin metal films. The solid samples, however, overcome the problem of short sample lifetime associated with irradiating thin films. Samples have been irradiated for several hours without observing a change in beam intensity or energy, thus offering an interesting source for kinetic studies. Initial results of studies done on copper, nickel, zinc and related oxide, sulfide, bromide, and chloride salts will be discussed as to their applicability to serve as a fast atom source. Spectroscopic data from these compounds will also be presented.

INTRODUCTION

In this work, the authors have found three characteristic areas of particle generation when using intense pulsed laser radiation. Early work on the interaction of high-power laser radiation with solids has been summarized by Ready¹ and Demichelis². At low laser power densities, $< 10^8 \text{ W cm}^{-2}$, the vaporization mechanism is local heating resulting in the production of neutral atomic and molecular species. Laser power densities $> 10^9 \text{ W cm}^{-2}$ result in plasma formation with high degrees of ionization and metastable formation of the vaporized species. The area between these demonstrates a combination of both phenomenon. For the application of this atom source in kinetic studies of neutral particle interactions, it is imperative to avoid the plasma regime since excitation of the species adds significantly to the complexity of the experiment.

This experiment was initiated to locate a appropriate source of fast metal atoms for hyperthermal chemical kinetic studies. Friichtenicht³ suggested the laser could be used irradiate a thin film of solid material to produce intense pulses of neutral atoms in the 1 - 10 eV range. He observed both the flux and the energy range of the atoms within the pulse could be varied within limits by adjusting the energy density of the laser light at the target surface. In order to efficiently use the laser energy for the production of neutral species, the targets bonded to optically transparent substrates were used. The laser beam was directed through the supporting material and focused on the rear side of the film. In this arrangement the hot plasma produced by the laser irradiation is physically constrained from expanding and the heat is more efficiently conducted from the plasma to the remaining solid material. He found that the maximum neutral atom flux obtained with the rear film bombardment geometry exceeded that of the solid target by about a factor of ten and that of the front film bombardment by a factor of four. The laser powers used in his experiment ranged from $1.8 \times 10^8 \text{ W cm}^{-2}$ for uranium to $1.33 \times 10^9 \text{ W cm}^{-2}$ for fluorine in a BiF_3 substrate. The sample lifetime, however, was short, lasting only 400 - 500 laser shots.

In this work it is suggested that the low bulk sample intensities are due to the rapid heat dissipation of the laser radiation into the bulk sample. We therefore proceeded to

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irradiate metal compounds due to their much lower thermal conductivity as compared to the base metal. In the three cases studied, copper, nickel, and zinc, we find a 3-20 fold increase in neutral metal atom intensity using compounds over bulk metal samples. Results of this experiment on the transition metals together with their related oxide, sulfide, chloride and bromide compounds will be compared on the basis of relative intensity, energy tunability, and neutral atom energy.

EXPERIMENTAL

The mass spectrometer has been described previously and will be outlined briefly.^{4,5} The mass spectrometer consists of three chambers, the source chamber, the ionization chamber, and the mass filter/ion detection chamber. The source and ionization chamber are evacuated by 4- and 8-inch cryopumps; the mass filter/ion detection chamber by an ion pump. Pressures in all chambers are maintained in the mid to low 10^{-8} torr region.

The source chamber consists of a X-Y movable sample platform. A Nd:YAG laser operating at 532 nm (2nd harmonic) irradiates the solid sample surface and vaporizes a small fraction of the sample. The laser typically operates with variable energy pulses up to 160 mJ which corresponding to $\approx 4 \times 10^5$ W cm⁻². Laser light is directed onto the sample through a series of five prisms. Laser energy reaching the sample surface is varied using a polarizer positioned prior to the first beam directing prism. The repetition rate is variable up to 10 Hz. The vaporized, neutral atoms travel a 27.9 cm flight path to an electron impact ion source where the ionized atoms are accelerated by a 4500V potential drop. Metastable formation is detected in this experiment by turning off the filament but leaving the repelling voltage on. Ions are repelled by the 4500V but neutral metastable atoms are allowed into the acceleration region where they are field ionized and show up in the TOF spectra as ultra-fast (> 30 eV) atoms. The ions are mass selected by a 60°, 12-inch radius magnetic mass filter and are detected by a microchannel plate (TOF-2003, Galileo, Inc). Time-of-flight measurements are started by a TTL pulse from the laser's Q-switch. Spectra are recorded and displayed on a multichannel scaler (SRS-430 Stanford Research Systems, Inc.)

RESULTS

A solid zinc sample was used to produce a pulsed atom beam but the intensity decreased quickly with time. One possible explanation is a thin oxide coating may have been present being preferentially vaporized due to a lower thermal conductivity. Once this layer was removed exposing zinc metal itself the heat spread quickly into the sample decreasing the amount of vaporization occurring. To test this theory, zinc oxide was vaporized using the same method. The zinc oxide provided a more intense Zn atom signal for a longer period of time than the zinc metal. Other zinc compounds were subsequently tested to determine which would give the most intense zinc atom signal. Time-of-flight spectra for the zinc compounds at laser power 3×10^5 W cm⁻² accumulated over 300 laser shots can be seen in Figures 1 through 4. The time-of-flight spectra show both ZnO and ZnS providing up to four times the signal level of the Zn metal itself. The Zn atom's energy is also greater and both ZnO and ZnS displayed an energy tunability with laser power as displayed in Table I. ZnBr₂ irradiation resulted in intensity levels less than the zinc metal. This, combined with the difficulty of working with an extremely hydrophilic material precludes its use as a zinc atom source.

The particle energy at peak TOF intensity over a range of laser powers can be seen in Table I. Values presented in bold are the result of ionic or metastable species present in the atom beam. Similar tests were completed for a series of copper and nickel compounds with similar results although not all compounds displayed the same neutral atom energy variability as the ZnO and ZnS samples had.

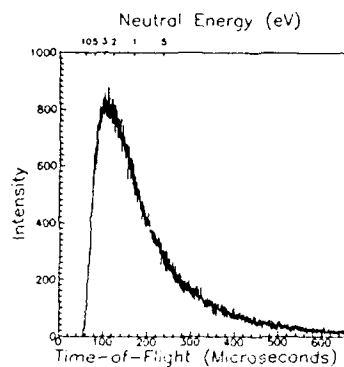


Figure 1. Zn TOF Spectrum Using Zn

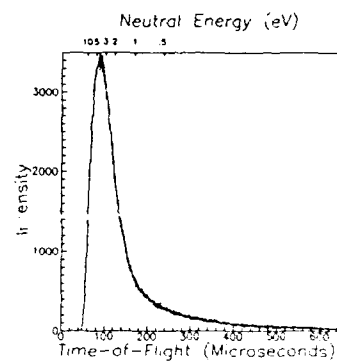


Figure 3. Zn TOF Spectrum Using ZnS

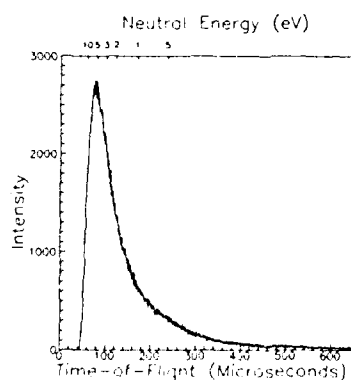


Figure 2. Zn TOF Spectrum using ZnO

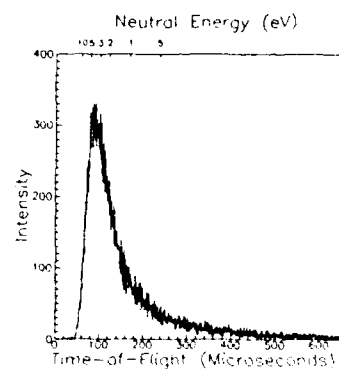
Figure 4. Zn TOF Spectrum using ZnBr₂

Table I.
Metastable/Neutral Atom Energy (eV) at Peak Intensity for Zinc Compounds

Laser Power (W cm ²)	Zn Metal	ZnO	ZnS	ZnBr ₂
1.8×10^9	56.0 / 15.7	-- / 6.8	-- / 6.7	-- / 4.6
7.2×10^8	-- / 2.8	-- / 4.4	-- / 5.2	
3.9×10^8		-- / 5.1	-- / 5.2	
2.1×10^8		-- / 2.9	-- / 2.6	
5.6×10^7			-- / 2.2	
2.0×10^7			-- / 1.7	

The copper compounds that were vaporized were CuO, Cu₂O, CuS, CuCl, and CuBr. TOF spectra from these compounds can be seen in Figures 5 - 10. The vaporization of the copper metal and copper compounds resulted in the formation of the ionic and metastable species, even at lower laser powers. Most evident is the ionic or metastable peak that is present in all but the CuO and CuBr spectra at $3 \times 10^8 \text{ W cm}^{-2}$. The intensity of this peak differs with the different compounds being most prevalent in the Cu₂O spectrum. The metastable formation is detrimental to the use of the specific compound in the hyperthermal experiment. None of the copper compounds displayed energy variability the ZnO and ZnS compounds had.

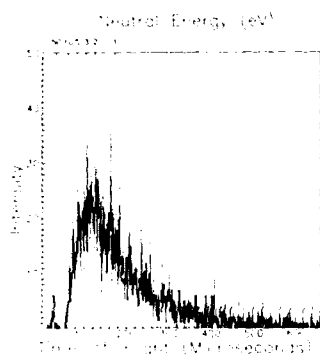


Figure 5. Cu TOF Spectrum Using Cu Disk

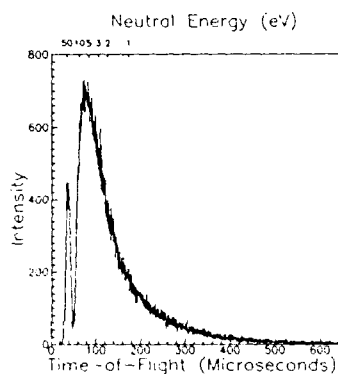
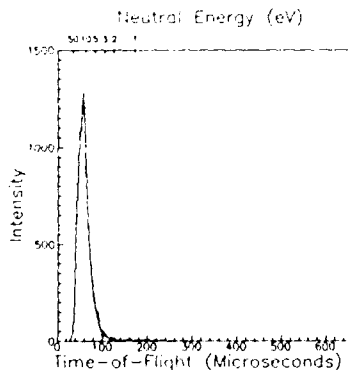
Figure 7. Cu TOF Spectrum using Cu₂O

Figure 6. Cu TOF Spectrum using CuO

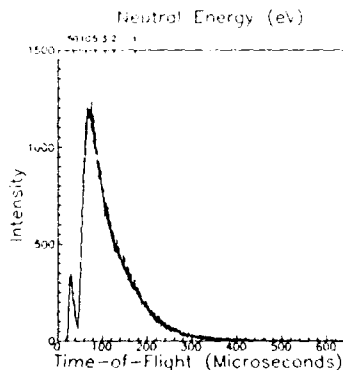


Figure 8. Cu TOF Spectrum Using CuS

Nickel, NiO and NiS pressed powder pellets were vaporized. The nickel samples had lower intensity than the zinc or copper samples but had much cleaner TOF spectra due to lower background for mass 58. NiO and NiS, similar to their related zinc compounds, displayed a tunability with laser power. Nickel TOF spectra using NiO and NiS are shown in Figures 11-12.

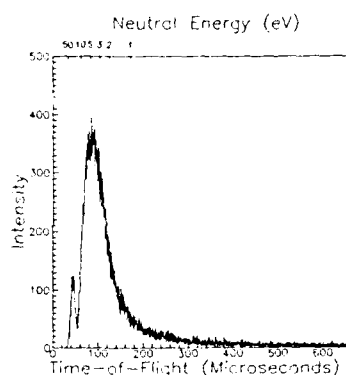


Figure 9. Cu TOF Spectrum using CuCl

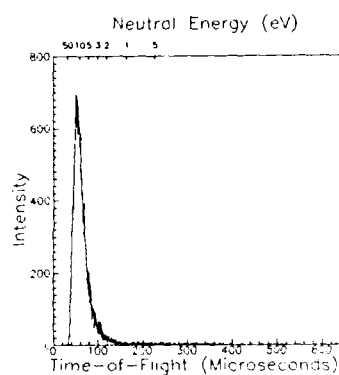


Figure 11. Ni TOF Spectrum using NiO

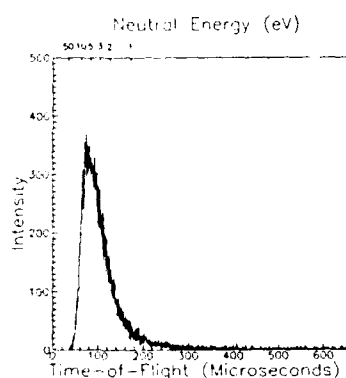


Figure 10. Cu TOF Spectrum using CuBr

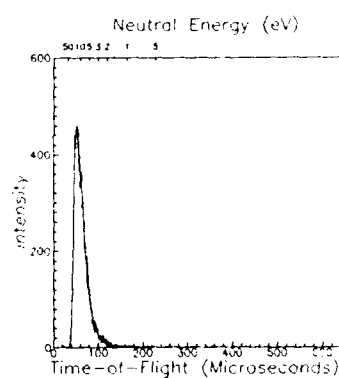


Figure 12. Ni TOF Spectrum using NiS

The addition of an optical multichannel analyzer to the sampling chamber allowed spectroscopic information to be gathered. Light produced by the vaporization process is directed through a fiber optic cable positioned above the sample surface. At low laser intensity ($< 5 \times 10^8 \text{ W cm}^{-2}$) neutral atom production is predominately in the ground state as demonstrated by the absence of any light coming from the sample. Increasing laser power produces excited energy states and eventually ionization of the vaporized species. A representative spectrum of ZnS vaporization at ($1.8 \times 10^9 \text{ W cm}^{-2}$) is shown in Figure 13 with spectral lines identified in Table II. The table displays that both excited neutral and ionic species are present in the vaporized material at this laser power.

Conclusion

It has been demonstrated that transition metal compounds can be used effectively in the production of neutral atom species, generating more intense neutral atom pulses than the metal species itself. In addition, sample lifetime greatly exceeds that of thin films. Tunability of the atom's energy with laser power allows the method to be used as a possible source for kinetic studies. A more comprehensive description of this experiment will appear shortly.

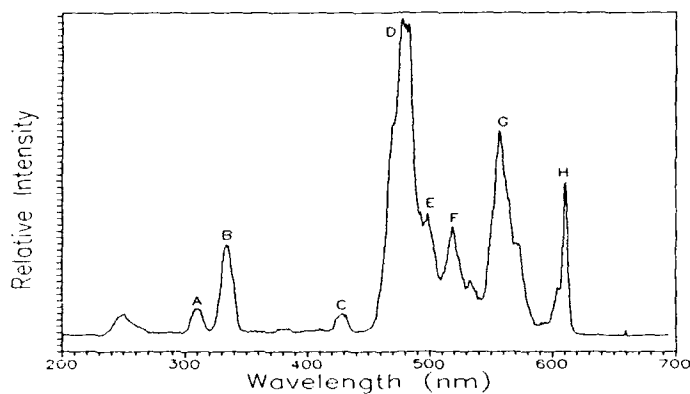


Figure 13. Optical Spectrum for Vaporization of ZnS
Laser Power $1.8 \times 10^7 \text{ W cm}^{-2}$
30 Second Integration Time (300 Shots)

Table II. Identified Spectral Lines from Figure 13

Label	Line (nm)	Element	Label	Line (nm)	Element
A	307.2	Zn(I)	D	468.0	Zn(I)
	307.5	Zn(I)		472.2	Zn(I)
B	328.2	Zn(I)		481.1	Zn(I)
	330.3	Zn(I)	E	491.2	Zn(II)
	334.5	Zn(I)		492.4	Zn(II)
C	414.2	S(II)	F	518.2	Zn(I)
	414.5	S(II)	G	545.4, 547.3	S(II)
	415.3	S(II)		551.0, 560.6	S(II)
	416.3	S(II)	H	602.1, 610.3	Zn(II)

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